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Thermoluminescence Characteristics of ZnS\CdS\ZnS Window Multilayer Thin Film for Solar Cell Applications

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Abstract

ZnS/CdS/ZnS multilayer thin film have been prepared by vacuum deposition method and studied using Thermoluminescence (TL) technique in order to investigate the defect structure in these films and the effect of chemical treatment in $CdCl_2$ and heat treatment on the defect structures . A series of electron and hole traps are found in the various deposited samples studied. After treatment, perturbation on the intensity is noted; mobile defect states and charge conversion and/or transfer between defect states are found.

Keywords:Thermoluminescenc; Defect; Glow Curve; ZnS/CdS/ZnS; Chemical treatment ; Thermal treatment; Thin film; Vacuum deposition; Solar cell.

1. Introduction

Thermoluminescence (TL) is the thermally stimulated emission of light from a semiconductor or an insulator when heated, after it had previously absorbed energy from a radiation source [1]; the phenomenon is observed through two consecutive processes: first when a system is exposed to an external excitation source of energy greater than the band gap, the system is perturbed and transferred from

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equilibrium into metastable states (defects in our case) by the absorption of energy from the ionizing radiation. This energy is stored throughout the process of electron-hole production, and exciton creation is followed by charge localization (trapping) at defect sites within the host lattice in the forbidden band, until equilibrium is achieved.

The second process is heating up the system linearly ($T=T_o+\beta t$), where the stored energy is released; thus, the electrons within traps are excited to the conduction band, and a fraction of these excited electrons are recombined; energy then appears in the form of luminescence (which is detected as light signal). On the other hand, retrapping processes occur to other excited electrons; the recorded intensity (emitted photons /s) versus temperature is called a "glow curve". Upon analyzing these and their distribution within glow curves, one obtains several and important information about the defects in the material, (activation energy, kinetic order and frequency factor) [2].

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This study concerns $Cd_{1-x}Zn_xS$ thin films, which are known to have properties between those of ZnS and CdS; by the addition of ZnS, the band structure of $Cd_{1-x}Zn_xS$ would have a larger energy gap than CdS which has energy gap of 2.42 eV. In other words, this hexagonal $Cd_{1-x}Zn_xS$ ternary compound becoming transparent to practically all wavelengths of solar spectrum and as results, it is potentially useful as window material for the fabrication of p-n junctions with minimum lattice mismatch in the devices [3,4]. $Cd_{1-x}Zn_xS$ can be prepared by a variety of techniques, including spray pyrolysis, ion beam deposition, molecular beam epitaxial growth, chemical bath deposition, thermal evaporation, and screen printing methods[5].

2. Experimental methods

In the preparation of our $Cd_{1-x}Zn_xS$ window, a 0.03-μm thick CdS film, sandwiched between two 0.04-μm-thick ZnS films, was first deposited onto Quartz substrates by vacuum deposition with a typical working pressures of 10^{-4} Pa were used during evaporation, this was then dipped in 1% $CdCl_2$ methanol solution for about 30 s to improve the conductivity, then dried with an infrared lamp and then rinsed in the deionized water then samples were annealed in air at 400 °C for 15min. Finally, all the produced samples were irradiated using α-source (2 MeV) for 30 min.

The TL response curve was measured using Pitman "TOLEDO" TLD-654 READER; the removable stainless steel tray in the sample drawer was used to set the detector to its readout position. After the drawer was closed the irradiated sample is heated by an electromechanical lift.

The Multi Channel Analyzer (MCA) is setup to Multi Channel Scaling (MCS) mode, intensity versus time. The data logger sensor, a linear temperature program, is also setup to measure temperature versus time simultaneously, when the annealing process is started with heating rate 2.0 Ks^{-1}, the data logger of the sample was also recorded. The process is terminated after 3 minutes and the data of the glow-peak are transferred to IBM computer using Xtalk program to save the data. The data were then plotted and analyzed using PEAK FIT with special TL function to extract the glow curve; other word deconvolution of the GL-curves was used to separate the overlapping dosimetric peaks and have the parameters (E, S, b and T_m).

3. Results and discussion

Thermoluminescence GL-curves generally give useful information about charge release mechanisms and recombination processes at the defect sites that are present within a material [6]; typical GL-curves obtained from the structure of ZnS\CdS\ZnS samples are shown in Fig.1; before and after chemical treatment in $CdCl_2$.

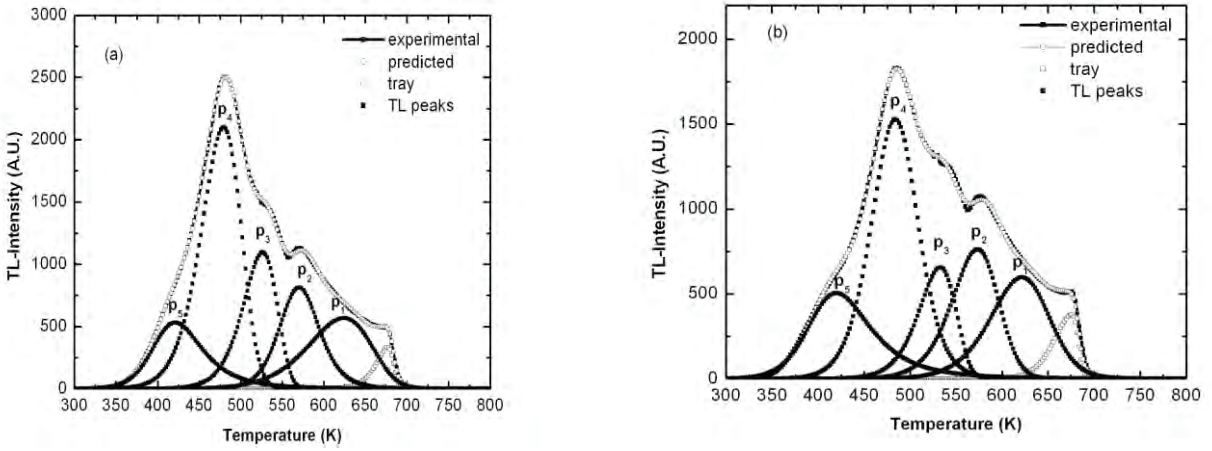

Fig. 1 Glow curve of ZnS\CdS\ZnS thin films: (a) before chemical treatment, (b) after chemical treatment.

Careful investigation of these GL-curves before chemical treatment indicates that the samples exhibit five main glow peaks centered at approximately 351°C, 297°C, 253°C, 206°C and 148°C, with shapes and glow peak intensities of considerably different strengths that vary from one to another. The intensity of TL signal produced in samples prepared via vapor deposition, strongly depends on thin film production conditions. Clearly, after chemical treatment (the concentration of Cl impurities in the samples increases), the intensity, the activation energy, the kinetic order parameter, and the peak temperature of TL signal reveal a clear change. For example, the intensity of most TL-peaks shows a decrease by 11%, 4%, 41%, and 22% for P_1, P_2, P_3, and P_4 respectively; P_5, on the other hand shows an exception and increase by 7%. It is also obvious that P_1 and P_5 indicate shifts towards lower temperatures while P_2, P_3 and P_4 exhibit shifts towards higher temperatures. The activation energy of most TL-glow peaks was also found to increase after this process.

It is well known that thermal treatments strongly modify the aggregation state of the impurity in the host lattice along with the existing traps within the material. In this respect, it is reasonable to assume that variations in the aggregation state of the impurity and its interaction with defects, defect clusters or dislocations reduce the number of traps that were present within the material before annealing. Fig.2 represents the Glow curve of our sample after annealing at temperature of 400C for 15 min.

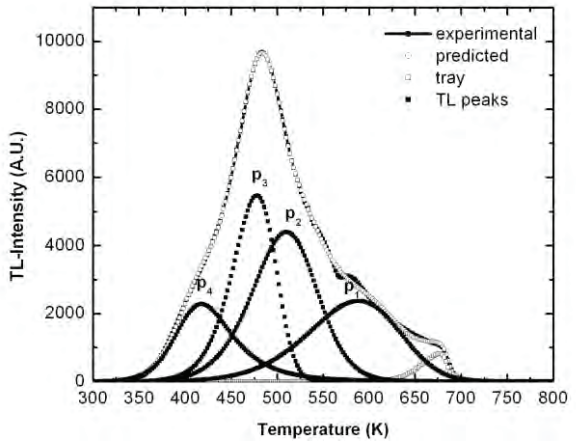

Fig. 2 Glow curve of ZnS\CdS\ZnS thin films after thermal treatment.

Compatible with this, only four glow peaks are identified after annealing between 417K and 589K; with a clear shift in the center of peak positions P_1, P_2, P_3, and P_4 towards low temperatures by some 5%, 11%, 10% and14% respectively. In addition, the large increase appears in the initial concentration of trapped electrons within the defects by some 506%, 705%, 873% and 92% for P_1, P_2, P_3, and P_4 respectively. Compared to data taken before treatment, the defect structure and states are mobile and a charge transfer between states may take place. As far as the activation energy is concerned, the peaks exhibit a decrease by 51%, 42%, 30 % and 24%, respectively, after annealing. Obviously, crystallinity of the produced samples increases after annealing and as a consequence of the distribution of energy levels of the present traps in ZnS\CdS\ZnS samples. It should also be noted that heat treatment induces defect migration and clustering that may cause an increase or decrease (via defect creation or destruction) in the trap densities and alterations in the electrically active states.

The CGCD method which uses the entire GL-curve to obtain the trapping parameters (table 1) indicate that the glow peak of produced ZnS\CdS\ZnS samples could not be successfully fitted with first-order kinetics. The program used, however, indicates that these peaks can be best fitted with first and general order kinetics. Accordingly, the kinetic order which is a measure of retrapping is affected by sample treatment conditions. One of the possible explanations of this result is to assume that the energy level of traps present in the samples are not single-level but instead have a distribution of energy levels [2, 7]. It is normally expected that high-temperature annealing or repeated heating runs dissolve the precipitated impurity and dissociate higher order impurity–vacancy complexes. Then, such traps can be filled during subsequent irradiation and therefore influence the shape and intensity of the GCs. In most TL materials redistribution of defects produces a large number of trapping and luminescence centers (such as vacancies and impurity related centers) in the lattice, which contributes to the increased intensity of TL GCs and therefore they are desirable due to their effect in increasing the efficiency and performance of the cells [6].

Another important factor that influences TL signal of the produced samples is the dopant or background impurities; it is well known that an impurity, such as oxygen is found as a background impurity in many

materials because of its diffusion properties into the crystal lattice during sample production or during the annealing stage in air at elevated temperatures [8]; in addition to the other residual impurity, Cl which was incorporated from the $CdCl_2$ solutions. Taking into account that the oxygen impurities are known to be first physically adsorbed at the grain boundaries and on the ZnS surface also, it acts as luminescent centers [8-10], and the presence of chlorine impurities in the ZnS thin films would be trapped in terms of Zn vacancy (V_{Zn})-Cl defects (V_{Zn}-Cl). These defects capture free electrons generated after irradiation by highly energetic particles (α-irradiation) and act as electron traps [11].

Table 1. Trapping parameters of ZnS/CdS/ZnS thin film by Computerized Total Glow Curve Deconvolution

	E (eV)	Tm(K)	b	n_0 (m^{-3})
P_1	0.579	588.569	1.079	150006
P_2	0.698	510.24	1.335	201123
P_3	0.840	477.97	1.11	167488
P_4	0.740	417.66	2.5	97904.9

4. Conclusion

ZnS\CdS\ZnS multilayer was deposited onto quartz via method based on chemical treatment and thermal processes that does not exceed 400 °C, is however, seen to have its potential impacts on solar cell industries. The influence of these treatments on the defects that were found in our films was investigated by using TL technique; the parameters of the identified traps, which appear a marked change after treatments, were also obtained based on kinetic analysis using CGCD method.

It was found that after thermal annealing, the initial concentration of trapped electrons within the defects centers strongly increases while the activation energy of TL signal decreases with loss of the low temperature electron traps, charge transfer and conversion between traps is noted.

Acknowledgements

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